

MECHANISMS OF FORMATION OF ANOMALOUS PHOTOINTENSIFICATION EFFECT IN Si/ORGANIC HETEROSTRUCTURES BASED ON PENTACENE AND CuPc LAYERS

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Abstract. This scientific work studies the photovoltaic processes in hybrid heterostructures formed by integrating organic layers such as pentacene and copper phthalocyanine (CuPc) into silicon (Si)-based semiconductor systems. The main focus of the study is on the theoretical and experimental analysis of the physical mechanisms of the anomalous photovoltage (APV) effect observed in these multilayer structures. As a result of the research, it was found that the singlet fission phenomenon occurring in the pentacene layer is of great importance. This quantum mechanical process ensures the conversion of one singlet exciton into two triplet excitons, significantly increasing the overall generation efficiency of charge carriers in the system. This, in turn, serves to increase the coefficient of conversion of solar energy into electrical energy.

The role of the CuPc layer in the heterostructure was studied in detail. It was found that this layer acts as a buffer that matches the energy levels, reduces the potential barriers between contacts and increases the internal electric field strength. This configuration allows for efficient charge separation and high photocurrent values. The results of the study serve as an important scientific basis for designing a new generation of hybrid photovoltaic devices with high efficiency.

Keywords: Si/pentacene/CuPc, hybrid heterostructure, anomalous photovoltage (APV), singlet fission, triplet excitons, charge carrier generation, energy levels, buffer layer, internal electric field.

INTRODUCTION

In modern optoelectronics, the anomalous photovoltage (APV) effect is of great importance in creating autonomous systems operating without an external power source. Unlike classical photocurrent, APV can occur in structures with internal asymmetry and provide a voltage exceeding the band gap. Since silicon (Si) has central symmetry, APV does not appear independently in it. Therefore, the necessary asymmetry and internal electric field are formed by creating hybrid heterostructures on the Si surface using organic semiconductors (pentacene and CuPc) [1]. In hybrid heterostructures based on silicon and organic semiconductor materials, effective separation of

photogenerated charge carriers as a result of interface charge redistribution and internal electric field formation has been observed. These processes are associated with the alignment of interface potential barriers and energy bands, and it has been shown that they can lead to an increase in photocurrent values [2].

Among organic semiconductors, pentacene and copper phthalocyanine (CuPc) materials are distinguished by their high photoactivity, selective transport of charge carriers, and high optical absorption coefficient. Pentacene is mainly used as a material that provides hole carrier transport, while the CuPc layer has the property of effectively generating photogenerated excitons and enhancing charge separation processes at the interface [3]. In heterostructures formed with the participation of these materials, the formation of anomalous photopower effects as a result of the formation of an internal electric field and the increase in the asymmetry of energy bands is likely to occur.

Recent modern studies have shown that in organic-inorganic hybrid structures, the photopower can be significantly increased due to the effect of interface dipoles and molecular polarization [1]. This expands the possibilities of creating new types of highly sensitive photodetectors and sensor devices operating without an autonomous energy source based on a combination of silicon and organic semiconductor materials.

The aim is to theoretically analyze the mechanisms of the formation of the anomalous photoexcitation effect in a hybrid heterostructure based on Si/pentacene/CuPc and to evaluate the influence of interface asymmetry, energy band matching, and exciton diffusion processes on the photoexcitation generation. A theoretical model based on exciton dynamics, charge separation at the boundary surface, and the generation of an internal electric field was developed to describe the mechanism of the anomalous photoexcitation (APV) effect in a Si/pentacene/CuPc heterostructure.

In organic semiconductor layers, photoexcitation mainly produces excitons, not free charge carriers. The migration of these excitons is controlled by a diffusion process and can be expressed by the steady-state diffusion equation:

$$D \nabla^2 n(x) - n(x)/\tau + G(x) = 0$$

where D is the exciton diffusion coefficient, τ is the exciton lifetime, and $G(x)$ is the rate of exciton generation upon illumination. The characteristic diffusion length is defined as $L = \sqrt{D\tau}$, which determines the probability of excitons reaching the boundary before recombination. The main feature of the pentacene layer is the presence of singlet splitting. In this process, a singlet exciton splits into two triplet excitons, effectively increasing the exciton population. This process, in turn, increases the density of long-lived triplet excitons, which have a high probability of diffusing towards the heterojunction.

Exciton dissociation at the Si/pentacene/CuPc boundary occurs due to the difference in energy levels and internal electric fields. The resulting charge carriers are separated and contribute to the photocurrent. The photocurrent can be approximately expressed as:

$$V_{ph} \approx Kt/q \ln(G \cdot L/n_0)$$

where k is the Boltzmann constant, T is the temperature, q is the elementary charge, and n_0 is the equilibrium carrier concentration.

The internal electric field E_{int} in the heterostructure arises due to the bending of the valence bands and the interfacial dipoles formed by the CuPc layer. This field plays a decisive role in the separation and transport of charge carriers. The relationship between the electric field and the potential distribution is expressed as follows:

$$E_{int} = -dV/dx$$

The CuPc interlayer improves the energy level matching between pentacene and silicon, reduces recombination losses, and enhances the internal electric field. As a result, the exciton dissociation and charge separation efficiency increase.

Based on this model, the anomalous photovoltaic effect in the Si/pentacene/CuPc heterostructure can be explained as the result of the combined effect of (i) enhanced exciton generation by singlet decay, (ii) efficient diffusion of excitons to the interface, and (iii) strong internal electric fields facilitating charge separation. This concept provides a coherent theoretical basis for analyzing the enhancement of photocurrent in hybrid organic–inorganic systems.

RESULTS AND DISCUSSION

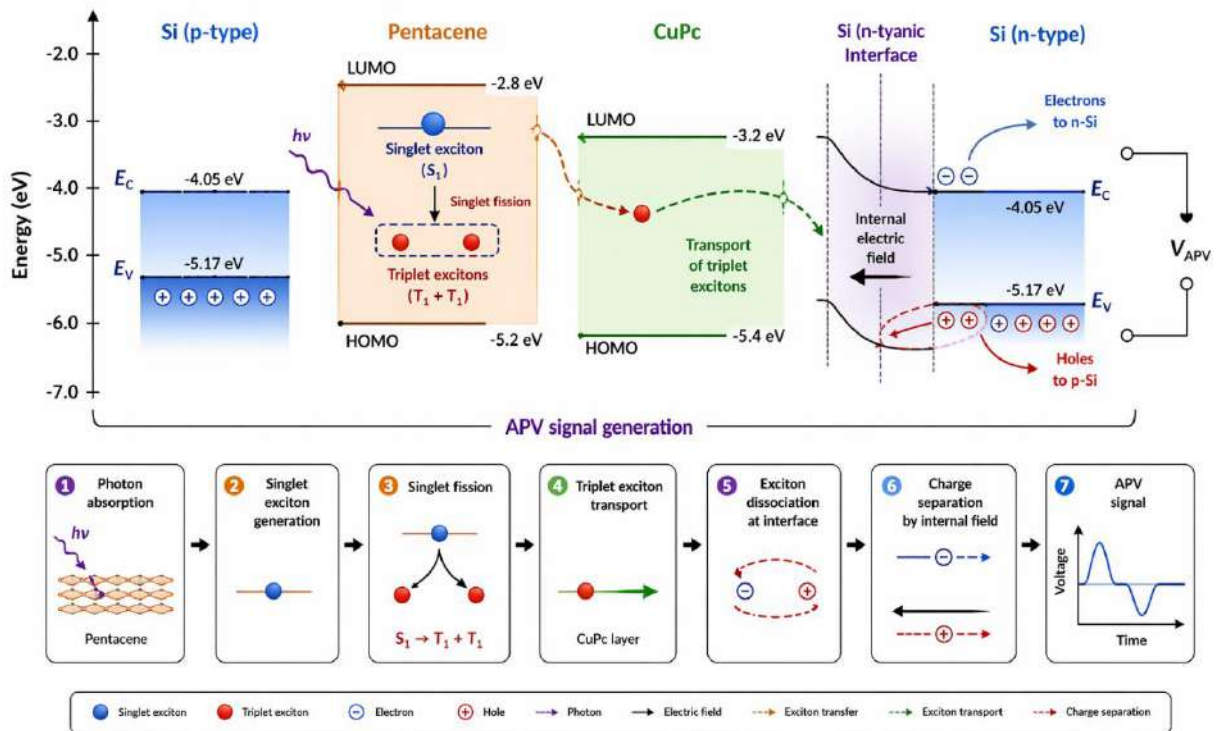
The mechanism of anomalous photovoltage (APV) generation in the Si/pentacene/CuPc heterostructure can be explained consistently within the framework of the proposed theoretical framework by linking the processes of exciton dynamics, singlet decay and interfacial charge separation. The presence of the CuPc layer is important in all stages by improving the matching of energy levels and introducing interfacial dipoles. This leads to an increase in the applied electric field and increases the efficiency of exciton dissociation and carrier separation.

Since triplet excitons have a much longer lifetime than singlet excitons, they are more likely to diffuse to the interface region. This increases the probability of exciton dissociation and enhances the generation of free charge carriers in the interface region. As a result, the space charge field formed at the Si/interface boundary is more effectively formed. An additional internal electric field is formed inside the structure, which leads to an increase in the anomalous photocurrent signal [2]. The internal electric field generated as a result of this bending serves to separate the carriers generated under the

influence of light in opposite directions. As a result, photocurrent is observed even under open contact conditions. This is considered one of the main physical mechanisms of the anomalous photocurrent effect [3].

Another important feature of the structure considered in this work is that it integrates the physics of molecular excitons and the physics of semiconductor devices. The singlet fission processes occurring in the pentacene layer represent the mechanisms of energy conversion at the molecular level. However, the subsequent transport and dissociation of these excitons occurs in the Si/interface region.

In studies conducted by Japanese scientists, singlet fission processes in pentacene and tetracene-based systems were mainly studied from the perspective of spin-dynamic processes, in which the mechanisms of triplet pair formation were analyzed using spectroscopic methods [4]. Although these works deeply studied the exciton evolution and spin state changes at the molecular level, they did not consider silicon-based device structures or anomalous photovoltage effects. Therefore, the Si/pentacene/CuPc heterostructure proposed in this work can be considered as a new hybrid model combining molecular exciton physics and device-level photoelectric conversion processes. Based on the proposed model, the formation mechanism of the anomalous photovoltage effect can be explained through the following steps:



Picturte 1. Energy cycling mechanism in the Si/pentacene/CuPc system

Table 1. The role of individual layers in the emergence of anomalous photocurrent in the Si/pentacene/CuPc heterostructure

№	Layer	Physical role	AFN contribution
1	Si	Charge separation field	Generation of internal electric field
2	Pentacene	Singlet fission generator	Triplet exciton propagation
3	CuPc	Interface smoothing layer	Energy level alignment and dipole formation
4	Region of Interfaces	Region of Space Charge	Enhancement of Carrier Dissociation

Another important factor that leads to the enhancement of the anomalous photoexcitation effect in Si-based structures is the presence of interface surface states. These surface states serve as additional charge traps under the influence of light and enhance the temporary charge separation. As a result, the potential gradient formed inside the structure increases, which leads to an increase in the APV signal [5].

In addition, the sequential arrangement of organic layers creates internal asymmetry within the structure. It is known that for the anomalous photoexcitation effect to occur, macroscopic asymmetry within the structure is necessary. The fact that the Pentacene and CuPc layers have different energetic and morphological properties creates an additional potential gradient within the structure. This is one of the main factors leading to the enhancement of the anomalous photoexcitation effect [5].

The results show that in Si/pentacene/CuPc-based heterostructures, the anomalous photovoltage effect can be significantly enhanced due to the interaction of singlet fission processes, interface energy matching, and internal electric fields. These results expand the possibilities of using the proposed structures in creating highly sensitive photodetectors operating without an external energy source and new generation hybrid photovoltaic devices.

CONCLUSION

The introduction of the CuPc layer not only improves the matching of energy levels within the heterostructure but also ensures a more efficient alignment between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the organic components and the conduction and valence bands of silicon. This optimized alignment significantly facilitates charge carrier transfer processes, reducing recombination losses and enabling a more effective separation of photogenerated electron–hole pairs at the interface.

As a consequence of this improved interfacial interaction, an additional interfacial dipole moment is formed, which arises due to charge redistribution and polarization effects between pentacene and CuPc molecules in contact with the silicon substrate. The presence of this dipole layer leads to a modification of the potential barrier at the interface, resulting in a strengthening of the built-in electric field within the heterostructure. This enhanced internal electric field plays a crucial role in accelerating charge carrier transport and extraction, thereby contributing to an increase in the overall efficiency of photoresponse.

Furthermore, the strengthening of the internal electric field directly influences the anomalous photovoltage effect, leading to its amplification. The enhanced photovoltage response is particularly important in low-light conditions, where traditional photovoltaic structures often suffer from reduced sensitivity and efficiency. In this context, the CuPc interlayer acts as an active functional component that not only improves charge dynamics but also stabilizes the electronic properties of the heterojunction.

The possibility of enhancing the anomalous photointensification effect based on the proposed Si/pentacene/CuPc heterostructure is of considerable scientific and practical significance. From a scientific perspective, it provides deeper insight into interfacial phenomena in hybrid organic–inorganic systems, especially regarding charge transfer mechanisms, dipole formation, and field-induced effects. From a practical standpoint, this approach opens new opportunities for the development of next-generation hybrid photovoltaic devices with improved efficiency, sensitivity, and operational stability.

In addition, such heterostructures can be effectively utilized in the design of highly sensitive optical sensors, capable of detecting weak optical signals with enhanced accuracy. They are also promising for the development of low-power, autonomous optoelectronic systems, where energy efficiency and compactness are important factors. In general, the integration of SuPc into silicon-organic hybrid structures is a promising direction of modern optoelectronics, combining the advantages of organic semiconductors (flexibility, elongation properties) with the strength and reliability of inorganic materials such as silicon.

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